

AFRL-RZ-WP-TR-2010-2078

NATIONAL AEROSPACE FUELS RESEARCH COMPLEX

Tim Edwards

Fuels and Energy Branch Energy/Power/Thermal Division

MARCH 2010 Final Report

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14. ABSTRACT

This report summarizes extensive in-house research performed by the Air Force Research Laboratory/ Propulsion Directorate Fuels Branch for the 2000-2009 time period under in-house work unit 304805F1. This work was organized under the organizational umbrella of the National Aerospace Fuels Research Complex (NAFRC). This in-house work unit is a successor/consolidation to a number of in-house work units, such as 30480537, 30480587, 2308P700, and is the predecessor to 5330SBF1. This work unit covered the time period from 2000-2009, and includes all the in-house efforts supporting the Fuels Branch of the AFRL Propulsion Directorate. The major on-site contract support was provided by the University of Dayton Research Institute through contracts F33615-97-C-2719 and F33615-03-2-2347. Approximately 60 on-site contractors work on this in-house program as of March 2010. This summary includes a general description of the in-house work areas – a more complete description will be found in the final report for F33615-03-2-2347, forthcoming in early 2011. Areas discussed in some detail include endothermic fuels, fuel hydrocarbon class analysis, and jet fuel naphthalene analysis.

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1.0 SUMMARY

This report summarizes extensive in-house research performed by the Air Force Research Laboratory/Propulsion Directorate Fuels Branch for the 2000-2009 time period under in-house work unit 304805F1. This work was organized under the organizational umbrella of the National Aerospace Fuels Research Complex (NAFRC).

2.0 INTRODUCTION

This in-house work unit is a successor/consolidation to a number of in-house work units, such as 30480537, 30480587, 2308P700, and is the predecessor to 5330SBF1. This work unit covered the time period from 2000-2009, and includes all the in-house efforts supporting the Fuels Branch of the AFRL Propulsion Directorate. The major on-site contract support was provided by the University of Dayton Research Institute through contracts F33615-97-C-2719 and F33615-03-2-2347. The publications for this in-house program are mostly included with the reports for the two UDRI contracts – there are hundreds! Approximately 60 on-site contractors work on this in-house program as of March 2010. This summary includes a general description of the in-house work areas – a more complete description will be found in the final report for F33615-03-2-2347, forthcoming in early 2011.

3.0 METHODS, ASSUMPTIONS, AND PROCEDURES

The Fuels Branch treats in-house research as an integrated part of the overall AFRL fuel research effort. Fuel Branch funding goes to various research areas which may include both in-house and contracted efforts. External funding is actively sought in most areas. The Fuels Branch also acts as a clearinghouse for research samples of aerospace fuels.

4.0 DISCUSSION

Fuels in-house efforts were managed as portfolios, and results will be summarized for each effort.

1) Thermal stability/thermal management

In the 1990s, the major development in this area was the first JP-8+100 additive. In the next decade (for this current report), DESC co-funded an effort develop further +100 additives for cost reduction. Four additives were developed for further testing. RZPF's in-house efforts included thermal stability testing. Testing of the second wave of JP-8+100 additives is still underway (March 2010). Results will be reported under F33615-03-D-2354-0015. An up-to-the-date summary of the JP-8+100 program can be found in AFRL-RZ-WP-TR-2008-2126 [1]. This portfolio also included extensive modeling and trace species assessment in jet fuels, e.g. [2]. These measurements are necessary for accurate thermal stability modeling, which is often controlled by trace species concentration in jet fuel. The following discussion is from Reference 2.

Aviation fuel is so complex that it is virtually impossible to separate all of the major components of the mixture, much less the minor components. The minor components are typically separated from the major components using preparative techniques (such as solid phase extraction, SPE) and then re-examined by gas chromatography-mass spectrometry (GC-MS). Without SPE, GC-MS is not capable of a comprehensive determination of the trace polar components in jet fuel due to fuel complexity. In the UDRI work for AFRL, jet fuel mixtures are pre-separated by normalphase SPE, followed by a single analysis using multidimensional gas chromatography-time of flight mass spectrometry (MDGC-TOFMS), which is similar to the recently popularized technique of GC X GC. This two-column sequential analysis followed by TOFMS identifications is able to accurately identify more of the polar components of jet fuel. Automated data analysis routines, based on improved mass spectral library identifications (due to the better chromatographic separations), are able to determine individual components in the polar fractions that are of interest. Spreadsheet-based sorting of the highest quality identifications was also performed and used to quantify important polar fuel classes such as amines, indoles, pyridines, anilines, sulfur compounds, oxygenates, aromatics, and others. These compound classes can have very different effects on thermal stability. The relative amounts of each group were determined and related to similar measurements found in the literature (see Table 1 and 2). The ability to identify and quantify polar components in fuel may be useful in developing relationships between fuel composition and properties such as thermal stability.

MDGC-TOFMS is an elegant way to identify and measure both individual compounds and compound classes in the polar fraction of jet fuel. These complex fractions are extremely difficult to measure by conventional GC-MS, except for the most abundant components. The measurements obtained did not agree quantitatively to existing HPLC compound class measurements. However, the two techniques did generally agree in a qualitative sense. The MDGC-TOFMS technique was shown to be a superior qualitative analysis technique compared to traditional GC-MS and HPLC. MDGC-TOFMS is also superior in trace analysis of complex mixtures because peak identifications can be made in an automated way with more confidence. Work is continuing to examine the complex results obtained; chemometrics and other statistical methods may be appropriate to apply to these measurements. In addition, improvement of the separations by changing columns, column lengths, phases, and other chromatographic

parameters is also possible. Distinguishing improvements achieved because of multidimensional separations versus improvements made due to TOFMS deconvolution needs to be performed to direct further experiments in this area.

Table 1. Classification of compounds using MDGC-TOFMS analysis compared to total HPLC polars analysis [2].

					v		·	
fuel	phenols (mg/L)	pyridine (mg/L)	carbazole (mg/L)	indole (mg/L)	amine (mg/L)	quinolines (mg/L)	sum of groups (mg/L)	HPLC polars (mg/L)
3084	92.8	4.4	0.1	2.7	6.7	0.8	106.6	
2985	736.4	540.4	0.2	57.1	65.4	87.6	1399.4	2400
3166	119.9	13.0	0.2	2.2	1.9	1.1	137.3	514
3603	< 1.0	0.7	0.1	0.5	0.5	0.7	2.5	110
3633	361.8	3.2	0.1	1.5	3.8	4.2	370.4	470
3658	200.5	507.3	3.0	63.3	133.6	60.4	907.8	2200
3684	21.2	0.5	0.1	0.8	0.6	0.8	23.2	240
3686	432.8	16.8	0.2	10.4	8.4	4.9	468.6	710
3688	199.9	37.3	0.3	6.6	15.8	6.1	260.1	510
3773	73.8	1.4	0.1	0.9	19.4	0.7	95.6	190
3804	37.0	0.0	0.1	0.7	0.6	1.5	38.5	190
4108	122.4	10.3	0.1	1.7	4.0	1.0	138.5	
4110	69.1	0.3	0.1	0.4	0.6	0.1	70.5	
4195	111.3	42.5	0.1	2.6	2.3	1.2	158.7	

Table 2. Library matches to various compound classes in jet fuels [2].

R.T. (s)	name	match quality of a possible 1	R.T. (s)	name	match quality (o of a possible 100
			1613.32	benzenamine, 2,5-dimethyl-	740
Phenols	Fuel Example 3166	0.40	1840.68	benzenamine, 2-ethyl-	933
688.08	phenol, 2,6-dimethyl-	940	1862.82	benzenamine, N,N,3,	774
790.14	phenol, 3-ethyl-	704	1002.02	5-tetramethyl-	//-
836.36	phenol, 2,3-dimethyl-	932	1000.19		021
897.2	phenol, 3,5-dimethyl-	933	1900.18	benzenamine, 3,5-dimethyl-	931
941.38	phenol, 2-ethyl-6-methyl-	916	1938.02	benzenamine, 2,3,4,5,	725
972.9	phenol, 3,4-dimethyl-	907		6-pentamethyl-	
984.6	phenol, 2-(1-methylethyl)-	881	1991.56	benzenamine, 2,3-dimethyl-	939
2001.78	phenol, 2,4,6-trimethyl-	909	2112.08	benzenamine,	769
2016.2	phenol, 3,4,5-trimethyl-	920		2-(1-methylethenyl)-	
2045.12	phenol, 2-propyl-	709	2124.2	benzenamine, 4-propyl-	884
2075.94	phenol, 4-(1-methylethyl)-	856	2168.26	benzenamine, 2-ethyl-6-methyl-	889
2092.18	phenol, 2,3,6-trimethyl-	927	2347.56	benzenamine, 2,6-diethyl-	729
2180.98	phenol, 4-propyl-	818	2450.84	naphthalenamine, tetrahydro-N,N-	
2195.62	phenol, 2-methyl-6-propyl	851	2430.64	dimethyl-	132
2211.3	phenol, 2-ethyl-5-methyl-	748	2514.56		725
2223.94	phenol, 2-(1-methylpropyl)-	918	2514.56	1-naphthalenamine, 5,6,7,8-	735
2225.28	phenol, 2,3,5,6-tetramethyl-	886		tetrahydro-	
2239.26	phenol, 2-methyl-5-(1-	732			
	methylethyl)-		Indoles	Fuel Example 3658	
2255.64	phenol, 2-ethyl-4,5-dimethyl-	860	2065.26	2-methylindoline	919
2314.78	phenol, 3-methyl-6-propyl-	839	2259.2	1H-indole, 2,3-dihydro-1-	849
2329.9	phenol, 4-(1-methylpropyl)-	793	2237.2	methyl-	047
2435.62	phenol, 3,5-diethyl-	779	2209.24	indole	926
2463.74	phenol, 2-(1,1-dimethylethyl)-5-	772	2308.34		
	methyl-		2505.1	1H-indole, 5-methyl-	922
481.82	2-allyl-4-methylphenol	796	2561.94	1H-indole, 3-methyl-	846
2555.56	2-ethyl-5-n-propylphenol	808	2565.48	1H-indole, 1-methyl-	871
2748.22	phenol, 2,5-bis(1-methylethyl)-	732	2580.18	1H-indole, 2-methyl-	864
2928.2	6- <i>tert</i> -butyl-2,4-dimethylphenol	719	2747.42	2H-isoindole, 4,7-dimethyl-	831
2974.02	3,4-diethylphenol	703	2830.7	1H-indole, 1,3-dimethyl-	863
		756		111 in dala 2.2 dimethyl	
079.92	phenol, 2-cyclohexyl-		2833.78	1H-indole, 2,3-dimethyl-	912
156.8	4-methyl-2-phenylphenol	777	2910.42	1H-indole, 5,6,7-trimethyl-	869
0-11	E1 E1- 2005		2984.28	1H-indole, 1,2,3-trimethyl-	871
Quinolines	Fuel Example 2985	724	2986.82	2,3,7-trimethylindole	702
2014.14	6-methyl-1,2,3,4-tetrahydroquinoline		2998.42	1H-indole, 2,3,5-trimethyl-	758
2171.76	quinoline	966	3030.14	1H-indole, dihydro-trimethyl-2-	803
2185.2	quinoline, 5,6,7,8-tetrahydro-	759		methylene-	
269.8	quinoline, 5,6,7,8-tetrahydro-3-	749	3162.48	2H-isoindole, 4,5,6,	803
	methyl-		3102.46		003
2303.38	quinoline, 1,2,3,4-tetrahydro-2-	799	2204.4	7-tetramethyl-	710
	methyl-		3294.4	ethanone, 1-(1,3-dimethyl-1H-	718
2327.92	3-ethyl-5,6,7,8-tetrahydroquinoline	726		indol-2-yl)-	
2349.7	quinoline, 2-methyl-	895	3311.16	1H-indole, 3-methyl-2-	716
2363.28	quinoline, 8-methyl-	798		propanoyl-	
2487.54	quinoline, 5-methyl-	899	3340.64	1,2,3,4,7-pentamethylindole	735
2503.32	quinoline, 3-methyl-	878	3388.5	1H-indole, 1-butyl-3-methyl-	807
2529.76	isoquinoline, tetrahydro-3-	826	3366.5	111-mdole, 1-outyr-5-methyr-	007
	methyl-		Carbazoles	Fuel Example 2985	
2559.96	dimethyl-1,2,3,4-	729			024
	tetrahydroisoquinoline		3674.3	carbazole	924
664.24	2,8-dimethylquinoline	805	3686.9	carbazole, 1,2,3,4-tetrahydro-3-	741
803.32	quinoline, 5,8-dimethyl-	704		methyl-	
856.98	dihydro-dimetquinolinylidene	733	3811.16	3-methylcarbazole	927
	methane		3917.12	carbazole, 1,6-dimethyl-	913
			3945.12	3-ethylcarbazole	740
Pyridines	Fuel Example 3658		4035.64	carbazole, 3,6-dimethyl-	913
252.16	pyridine, 2,4,6-trimethyl-	918	4064.36	carbazole, 2,5-dimethyl-	888
311.72	pyridine, 2,3,6-trimethyl-	836			
358.48	pyridine, 2-ethyl-6-methyl-	718	4123.34	carbazole, 1,3-dimethyl-	705
522.1	2-ethyl-3,5-dimethylpyridine	718 798	4125.88	carbazole, 2,4,6-trimethyl-	853
			4154.66	carbazole, 2,3,5-trimethyl-	868
535.68	pyridine, 2-ethyl-4,6-dimethyl-	740		-	
667.5	pyridine, 2-ethyl-6-isopropyl	812	Sulfur	Fuel Example 2985	
935.08	pyridine, 3-ethyl-5-methyl-	726	1631.96	cyclothiazide	596
134.16	pyridine, 2-methyl-4,6-dipropyl-	761		1.2-dithiane	
	pyridine, 4-methyl-2-(2-methyl-1-C3-		1968.46		924
227.72	tetrahydropyridine, 4-[4-	717	2376.54	benzothiazole	957
227.72 2658.18			3635.16	2-benzothiophene, dihydro-5,6-	743
	hydroxyphenyl]-				
658.18	hydroxyphenyl]- 2,4-dimethyl-6-phenylpyridine	769		dimethyl-	
658.18		769			
658.18 159.34		769		dimethyl- of compounds were taken from a partic	cular fuel, as not
	2,4-dimethyl-6-phenylpyridine	769 715			cular fuel, as not

2) Endo fuels and propellants

This portfolio includes efforts supporting endothermic fuels for hypersonics and hydrocarbon rocket propellants. In general, all of these studies involve the mitigation of coking under various

flow and temperature regimes [3,4]. On of the key aspects of this work is linking the chemical compound classes in jet fuels (Table 3) with coking behavior. This class analysis is discussed further below in section 3).

Table 3. Hydrocarbon-type composition for representative and test fuels by ASTM D2425 [11]

	World survey average, vol %	Composite Jet A blend (POSF4658)	Jet A-1 (POSF 4877)	JP-7 (POSF 3327)	F-T Jet A-1 (POSF 4820)
Paraffins (normal + iso)	58.8	55.2	64.2	67.9	> 99%
monocycloparaffins	10.9	17.2	13.5	21.2	< 1
dicycloparaffins	9.3	7.8	3.8	9.4	< 1
tricycloparaffins	1.1	< 1	< 1	< 1	< 1
alkyl benzenes	13.4	12.7	12.6	0.7	< 0.2
indans+tetralins	4.9	4.9	3.8	< 0.2	< 0.2
naphthalene	< 0.2	< 0.2	0.3	< 0.2	< 0.2
substituted naphthalenes	1.6	1.3	< 0.2	< 0.2	<0.2

^{*} The technique also measures acenaphthenes, acenaphthylenes, tricyclic aromatics, and indenes, but these were below detection limits in all cases.

As can be seen in Figures 1 and 2, Fischer-Tropsch fuels and conventional fuels can have very different reactivity (Figure 1) and deposition (Figure 2) behavior [4]. It was somewhat surprising that the deposition from the F-T was so much larger under pyrolysis conditions. Even when tests with equivalent conversions are compared (Figure 3), the F-T fuel is still a much higher depositor. The working hypothesis was that aromatic components in fuels were serving as growth sites for polycyclic aromatic hydrocarbons (PAH), the presumed precursors to deposit formation. Figure 4 shows that aromatic formation is indeed seen in typical jet fuels with a correlation to deposit formation, with PAH formation seen in Figure 5 in measurements by LSU (none of these PAH are detectable in the original fuel). However, the aromatic-free F-T fuels still form copious amounts of deposits (and PAH – Figure 6), so the initial steps of aromatic formation are obviously important and poorly understood. All of these coking tests were performed in-house – similar PAH formation is seen in tests performed with F-T at UTRC (Figure 7) and LSU (Figure 8) – so the data is not an artifact.

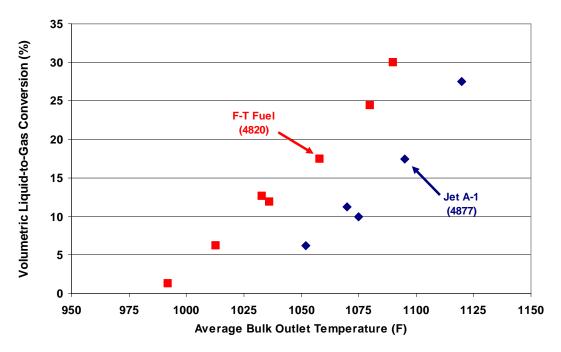


Figure 1. Comparison of the volumetric liquid-to-gas conversion as a function of the bulk outlet fuel temperature.

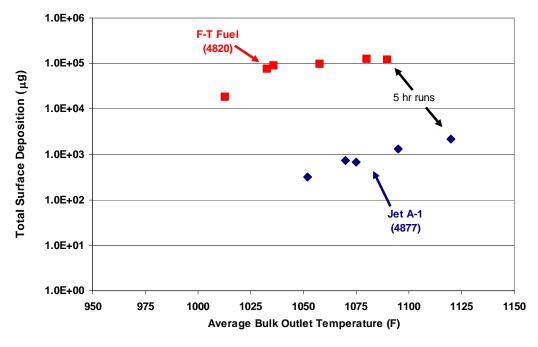


Figure 2. Comparison of the total surface carbon deposition for Jet A-1 and F-T fuels as a function of bulk outlet temperature.

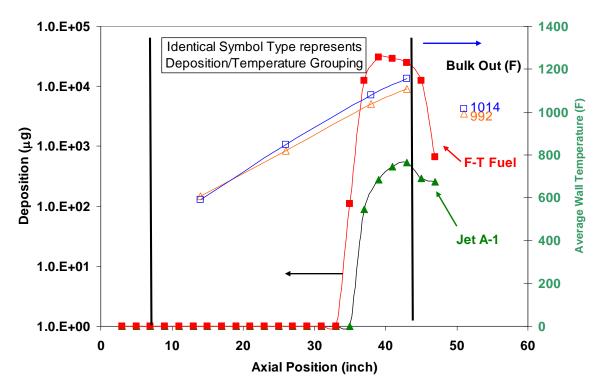


Figure 3. Comparison of the surface deposition profile for Jet A-1 and F-T fuels with ~18% gaseous product conversion.

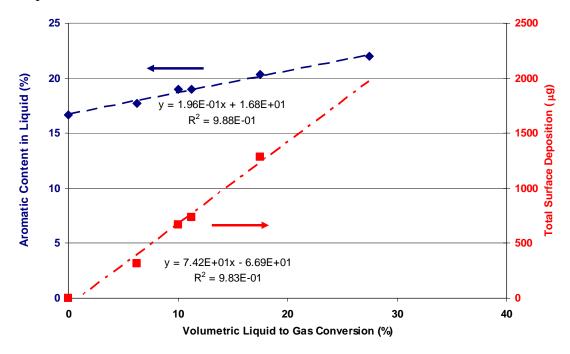


Figure 4. Comparison of aromatic content in stressed liquid and total surface deposition as a function of gas conversion for pyrolytic testing with Jet A-1.

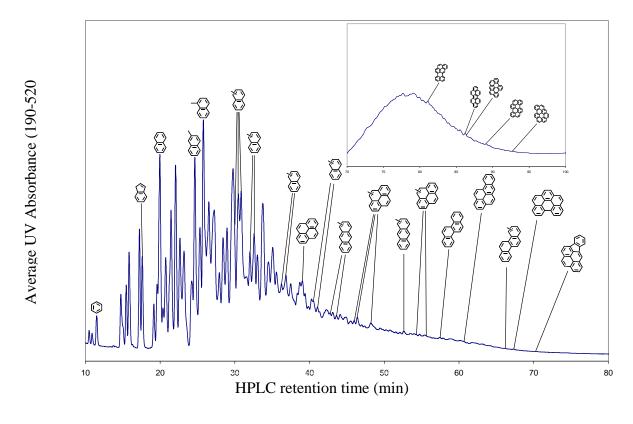


Figure 5. Representative chromatogram of stressed Jet A-1 liquid product from supercritical pyrolysis.

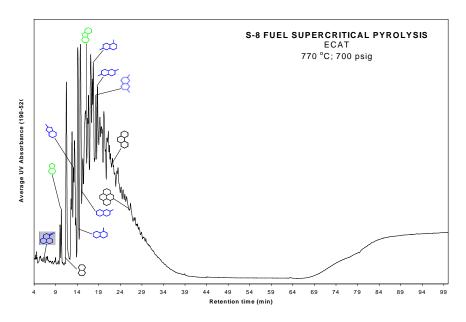


Figure 6. Representative chromatogram of low conversion stressed S-8 liquid product from supercritical pyrolysis on ECAT.

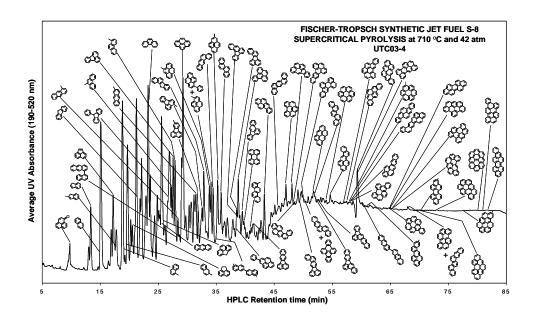


Figure 7. Representative chromatogram of very high conversion stressed S-8 liquid product from supercritical pyrolysis at UTRC.

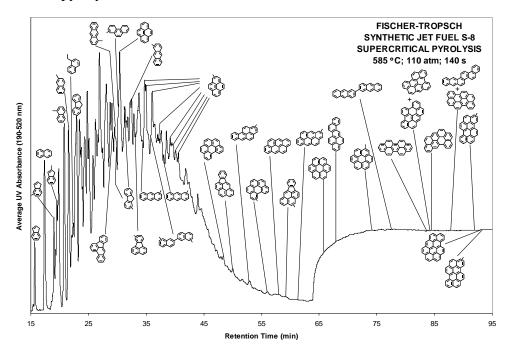


Figure 8. Representative chromatogram of stressed S-8 liquid product from supercritical pyrolysis at Louisiana State University.

3) Alternative fuels, fuel characterization

This portfolio supported studies of conventional jet fuel composition, as well as alternative fuels composition and properties, e.g. [11]. The in-house compositional analyses supported updates

of the JP-8 (MIL-DTL-83133F) and Jet A (ASTM D7566) specifications. The in-house effort also supported the development of MIL-HDBK-510, Alternative Fuel Certification. In support of the DARPA Biojet program, extensive compositional and property analyses were performed on biofuels, which led to the decision to certify hydrotreated renewable jet (HRJ). This AF effort will lead to flight demonstrations/tests in 2010, initially with the A-10 on March 25, 2010.

Typically the analysis focused on separating the thousands of hydrocarbons in typical jet fuels into classes. Occasionally, specific molecules are targeted. One interesting example was a request to quantify naphthalene ($C_{10}H_8$) levels in fuels due to potential toxicity issues. Linda Shafer of UDRI performed an extensive analysis of naphthalene levels in transportation fuels, to be described in detail in a forthcoming refereed paper. However, it is worth showing a few of the highlights. As shown in Figure 9, naphthalene and its derivatives fall within the typical molecular weight range of jet and diesel fuels. The total of naphthalene derivatives are typically characterized by ASTM D1840, and limited to 3 vol% in jet fuels. Often, this is mis-interpreted as 3% naphthalene ($C_{10}H_8$), which is incorrect. This research verified the levels of naphthalene and two derivatives in gasoline, diesel, and jet fuels samples world-wide (166 total samples). The results are shown in Table 4. For jet fuel, the 1+ vol% total naphthalenes (~10,000 mg/L) far exceeds the levels of the specific identified naphthalene isomers (~2000 mg/L typically). Also of interest was the distribution of naphthalene and its isomers (Figure 10) to verify if there were a few high-naphthalene fuels or if the distribution was more "normal".

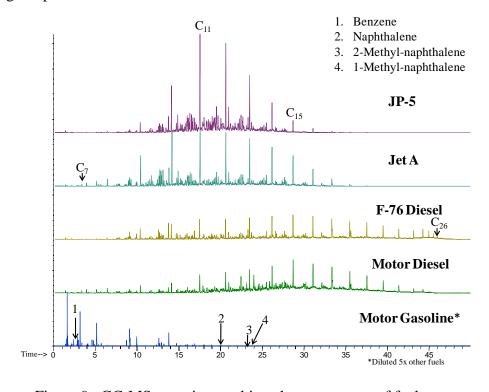


Figure 9. GC-MS scanning total ion chromatograms of fuels.

Table 4. Mean naphthalene content and standard deviation for fuel classes. It has been previously noted that the D6379 technique yields somewhat different values that D1840 [2].

Fuel	Naphthalene,	1-methyl	2-methyl	D1840total	D6379 total
	μg/mL	naphthalene,	naphthalene,	naphthalenes,	naphthalenes,
		μg/mL	μg/mL	vol %	vol %
Jet	1526±772	1525±495	2365±869	1.15±0.38	1.33±1.49
F-76	1587±599	1688±701	3008±1505	4.05±0.84	5.74±1.21
auto diesel	357±241	563±467	1047±875	2.61±1.01	3.19±1.48
gasoline	1484±797	467±319	1077±733	0.42±0.21	0.42±0.23
Jet [2,3]	1583±1037			1.23±0.72	1.80±1.00

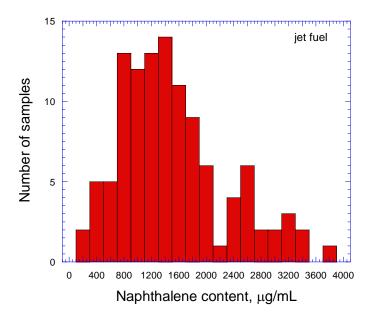


Figure 10. Distribution of naphthalene content in jet fuels from this study.

Also of interest was the relationship between the typical "total naphthalenes" test (ASTM D1840) and other tests that can report similar data, such as ASTM D6379. As shown in Figure 11, there is a good correlation at lower "naphthalenes" content, which breaks down somewhat at the upper end of the range. There was also interest in determining if concentrations of specific naphthalene isomers could be inferred from the total "naphthalenes" data. As shown in Figure 12, there is a correlation – but is does have a lot of scatter. The scatter is reduced somewhat when the jet fuels are divided up by type (Figurs 13 and 14), but the correlation is still not

predictive (note the scatter in the JP-8 points). So, for example, it is not possible to infer 1-methyl naphthalene content in JP-8 from the typical ASTM D1840 "naphthalenes" measurements – at least not to less than a factor of ~2 accuracy. It is interesting to note the correlation is much stronger for gasoline apparently, as shown in Figure 15 for naphthalene, Figure 16 for 1-methyl naphthalene, and Figure 17 for 2-methyl naphthalene.

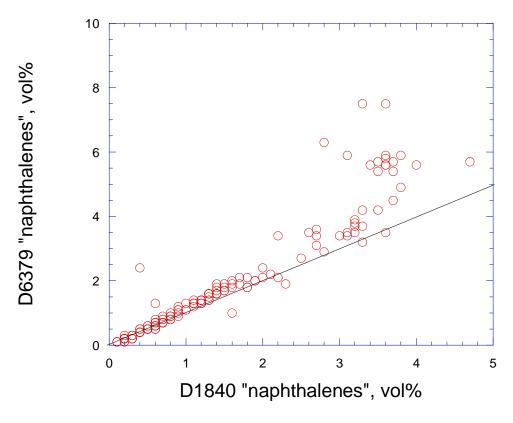


Figure 11. Correlation between total napthalenes by ASTM D1840 and D6379.

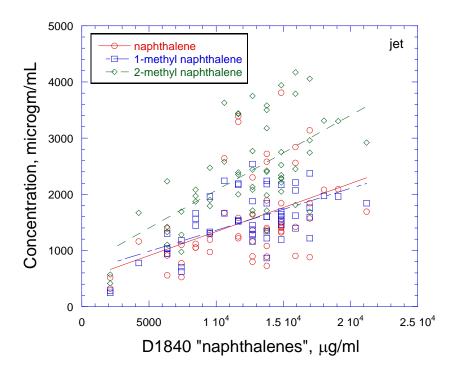


Figure 12. Relationship between total naphthalene content and individual naphthalene components for jet fuel samples.

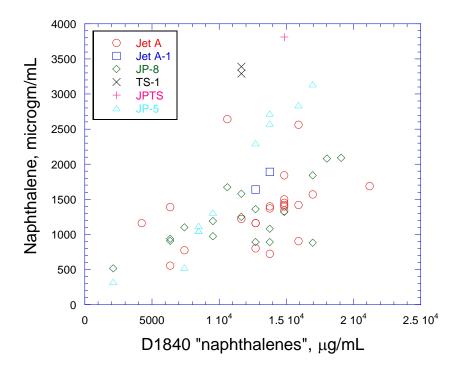


Figure 13. Naphthalene content as a function of jet fuel type.

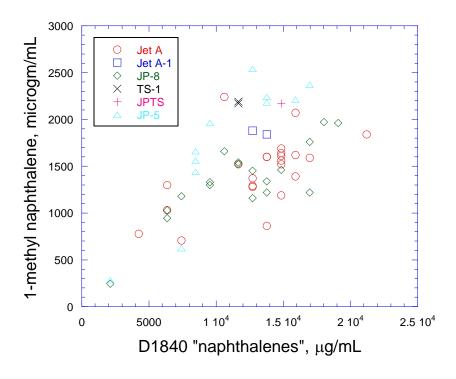


Figure 14. 1-methyl naphthalene content as a function of jet fuel type.

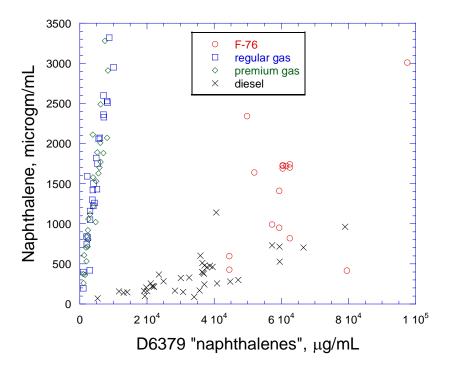


Figure 15. Naphthalene content for the four classes of ground fuels.

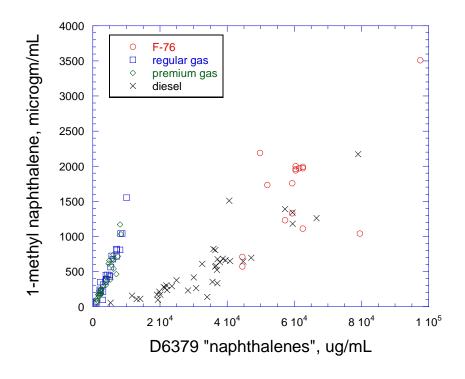


Figure 16. 1-methyl naphthalene content for the four classes of ground fuels.

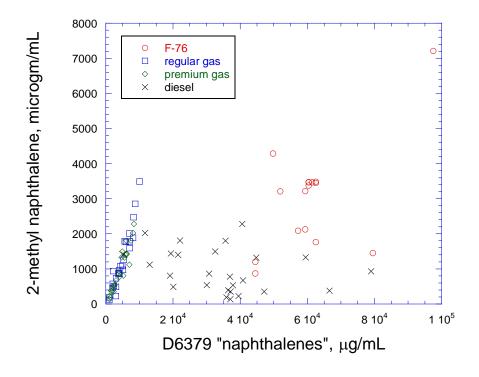


Figure 17. 2-methyl naphthalene content for the four classes of ground fuels.

4) Low temperature fuels

The in-house effort supported an ATD "JP-8+100LT Upgrade for the U-2 and Global Hawk". This ATD successfully developed an JP-8 additive package that enabled JPTS behavior in JP-8 [5,6]. This work was partially funded by the U-2 program office.

5) Fuel system icing inhibitor (FSII) studies

The current FSII in JP-8 (diethylene glycol monomethyl ether) is causing operational problems at its current usage level (0.1-0.15 vol % in MIL-DTL-83133F). RZPF evaluated both alternative FSIIs (such as triethylene glycol monomethyl ether) and lower levels of the current FSII to ensure that the effectiveness of the additive is maintained [7,8]. Flight tests involving both options are planned in 2010. Both biological growth mitigation testing (see 6) below) and component icing tests indicate that levels of the current FSII as low as 0.04 vol% are effective at mitigating biological growth and preventing icing – as well as preventing the material compatibility problems caused by FSII.

6) Biological growth in aviation fuels

This portfolio examined the current microbial growth issues in aircraft (largely mitigated by FSII) and studied alternative FSIIs and alternative fuels [9,10]. An ongoing AF effort to assess the use of commercial Jet A fuel instead of JP-8 is driving further research on biological growth mitigation.

7) Emissions Reduction via Fuel Technologies

This portfolio focused on state-of-the-art emissions measurements, focusing on particulates [12]. An extensive amount of effort was spent improving particulate measurement technology as part of a multi-agency group. For example, note the multiple agencies present at an aerial view of a January 2009 test in California sponsored by NASA and AFRL (Figure 18).

8) Nanofuels, nanoenergetics

This portfolio developed nano-particle solutions for fuel additives and energetic materials. A key aspect of the work was ensuring controlled reactivity as a function of temperature and air exposure [13-15]. This research enables new avenues for field hydrogen generation [16].

5.0 CONCLUSIONS

This large in-house effort has been a very productive part of the Propulsion Directorate in-house research effort.

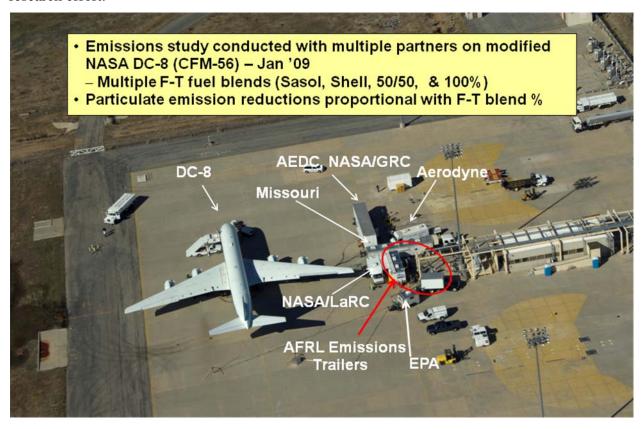


Figure 18. Aerial view of January 2009 aircraft emissions testing.

6.0 REFERENCES

- 1. Morris, R. W., et al, "JP-8+100 Current Knowledge and Best Practices," AFRL-RZ-WP-TR-2008-2126, April 2008.
- 2. Striebich, R. C., et al, "Identification of Polar Species in Aviation Fuels using Multidimensional Gas Chromatography-Time of Flight Mass Spectrometry," Energy Fuels 2009, 23, 5474–5482.
- 3. Edwards, T., "Cracking and Deposition Behavior of Supercritical Hydrocarbon Aviation Fuels," Combustion Science and Technology, Vol. 178, pp. 307-334, 2006
- 4. Edwards, T., DeWitt, M, Shafer, L., Brooks, D., Huang, H., Bagley, S, Oña, J., and Wornat, M. J., "Fuel Composition Influence on Deposition in Endothermic Fuels, AIAA Paper 2006-7973, November 2006.
- 5. R. Assudani, J.S. Ervin and S. Zabarnick, "Computational Fluid Dynamic Simulations of Jet Fuel Flow Near the Freeze Point Temperature," *Prepr.-Am. Chem. Soc., Div Pet. Chem.*, Vol. 49, pp. 502-505, 2004.
- 6. L.M. Shafer, J.S. Ervin and S. Zabarnick, "Effects of Low-temperature Additives on Phase Compositions of Jet Fuel," *Prepr.-Am. Chem. Soc., Div Pet. Chem.*, Vol. 49, pp. 506-509, 2004.
- 7. M.J. DeWitt, S. Zabarnick, T. Williams, Z. West, L. Shafer, R. Striebich, S. Breitfield, C. Delaney, and D. Phelps, "Determination of Minimum Required FSII Dosage for Use on USAF Aircraft," Proceedings of the 10th International Conference on Stability, Handling and Use of Liquid Fuels, 2007.
- 8. S. Zabarnick, Z. West, M.J. DeWitt, L. Shafer, R. Striebich, C. Delaney, and D. Phelps, "Development of Alternative Fuel System Icing Inhibitor Additives that are Compatible with Aircraft Tank Topcoat Material," Proceedings of the 10th International Conference on Stability, Handling and Use of Liquid Fuels, 2007.
- 9. Vangness, M., et al, "Biocontamination Diversity in JP-8 and Jet-A," Proceedings of the 11th International Conference on Stability, Handling and Use of Liquid Fuels, 2009.
- 10. Balster, L. M., et al, "Effect of FSII on Microbial Contamination in Jet Fuel; DiEGME and TriEGME," Proceedings of the 11th International Conference on Stability, Handling and Use of Liquid Fuels, 2009.
- 11. Shafer, L, Striebich, R., Gomach, J., Edwards, T., "Chemical Class Composition of Commercial Jet Fuels and Other Special.ty Kerosene Fuels," AIAA Paper 2006-7972, November 2006.
- 12. Corporan, E. et al, "Emissions Characteristics of Legacy Military Aircraft," ASME-GT-2009-59255, MISSIONS CHARACTERISTICS OF A LEGACY MILITARY AIRCRAFT, Proceedings of ASME Turbo Expo, June 2009.

- 13. Fernando, K. A. S.; Smith, M. J.; Harruff, B. A.; Lewis, W. K.; Guliants, E. A.; Bunker, C. E. "Sonochemical Assisted Thermal Decomposition of Alane N,N-Dimethylethylamine with Titanium (IV) Isopropoxide in the Presence of Oleic Acid to Yield Air-Stable and Size-Selective Aluminum Core-Shell Nanoparticles" J. Phys. Chem. C 2009, 113, 500-503.
- 14. Chung, S. W.; Guliants, E. A.; Bunker, C. E.; Hammerstroem, D. W.; Deng, Y.; Burgers, M. A.; Jelliss, P. A.; Buckner, S. W. "Capping and Passivation of Aluminum Nanoparticles Using Alkyl-Substituted Epoxides" Langmuir 2009, 25, 8883–8887.
- 15. Li, H.; Meziani, M. J.; Lu, F.; Bunker, C. E.; Guliants, E. A.; Sun, Y.-P. "Templated Synthesis of Aluminum Nanoparticles A New Route to Stable Energetic Materials" J. Phys. Chem. C 2009, 113, 20539-20542.
- 16. Bunker, C. E.; Smith, M. J.; Fernando, K. A. S.; Harruff, B. A.; Lewis, W. K.; Gord, J. R.; Guliants, E. A.; Phelps, D. K. "Spontaneous Hydrogen Generation from Organic-Capped Al Nanoparticles and Water" ACS Applied Materials & Interfaces 2010, 2, 11-14.

LIST OF ACRONYMS, ABBREVIATIONS AND SYMBOLS

<u>Acronym</u> <u>Description</u>

AF Air Force

AFB Air Force Base

AFRL Air Force Research Laboratory

ASTM American Society for Testing of Materials

ATD Advanced Technology Demonstrator/Demonstration

DARPA Defense Advanced Research Projects Agency

DESC Defense Energy Support Center (part of Defense Logistics Agency)

ECAT Estudios Combustibles y Altas Temperaturas (rig)

F-T Fischer-Tropsch

FSII Fuel System Icing Inhibitor

GC Gas Chromatograph

GC-MS Gas Chromatograph – Mass Spectrometer

HPLC High Performance Liquid Chromatography

HRJ Hydroprocessed Renewable Jet

JP-8 Jet Propellant 8

JPTS Jet Propellant Thermally Stable
LSU Louisianan State University

MDGC Multi-Dimensional Gas Chromatograph

MIL-HDBK-510 Military Handbook 510

NAFRC National Aerospace Fuels Research Complex

NASA National Aerospace Research Complex

PAH Polycyclic Aromatic Hydrocarbons

RZPF AFRL Fuels Branch (organizational symbol, not an acronym)

SPE Solid Phase Extraction

TOFMS Time-Of-Flight Mass Spectrometer

UDRI University of Dayton Research Institute

UTRC United Technologies Research Center